STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

6p.

January 15, 1964



Report No. 7
Final Summary Report [15 Apr. 1962 - 15 Jan. 1964]
No. 7

UNPUBLISHED PRELIMINARY DATA

# THEORETICAL RESEARCH--ELECTRONIC, IONIC, AND ATOMIC IMPACT PHENOMENA

By Felix T. Smith 15 Jan. 1964 6p refs

SRI Project PAU-4070

Prepared for:

Office of Research Grants and Contracts, Code BG
National Aeronautics and Space Administration
Washington 25, D.C.

[redacted]

(NASA Contract No. NASr-49(07))

Copy No. 2

# I INTRODUCTION

This investigation involves: (1) fundamental studies in the field of low energy electronic, ionic, atomic, and molecular impact phenomena, and (2) theoretical studies specifically related to our experimental investigations on low-energy collisions. Work in a closely related area is also being carried out under a grant from the National Science Foundation under the title, "Quantum Mechanics of Molecular Rearrangements."

This report summarizes the work done during the total contract period, April 15, 1962 to January 15, 1964, with additional emphasis on the work beginning October 15, 1963. Reference may be made to our quarterly reports* for further information on activities up to October 15, 1963.

# II THEORETICAL ACTIVITIES

For the past four years under the sponsorship of Stanford Research Institute, of NASA (under this contract and under contract NASW-80), and of NSF, we have been engaged in a number of studies related to the general area of the quantum mechanics of molecular rearrangements. The intention of this program has been to apply modern quantal collision theory to problems of chemical kinetics. The results of this program have appeared or will appear in the published literature and are briefly summarized here. In the course of the work we have had occasion to review the status of collision theory in chemical kinetics (in 1960),[1] to develop some new fundamental conceptual tools in collision theory (the lifetime matrix,[2] generalized angular momentum to describe 3-body and many-body collisions,[3,4] many-body collision lifetimes,[5] many-body Green's functions[6,7]), to show how these concepts can be applied in

*Quarterly Reports No. 1 through 6 under this project.

statistical systems (in the connections between collision properties and chemical reaction rates,[8] and between collision lifetimes and the thermodynamic functions of imperfect gases[9,10]), and to make use of the insights gained for predicting, correlating, and interpreting experimental results (in a classical approximation to the theory of 3-body reactions,[11] a quantal theory of 2-body collision lifetimes applicable to 3-body reaction rates,[12] and some new results in the theory of charge-exchange collisions at low energies[13]). Of these items, references 5, 6, 7, and 9 through 13 were supported in whole or in part by this project. During the last quarter, references 7 and 13 were prepared and copies of them are being forwarded separately. Reprints of reference 9 have recently been received and copies are also being forwarded separately.

In addition to these pieces of work, certain other items are currently in progress. Dr. Alan L. Stewart (on leave from Queen's University, Belfast) is working on the theory of configuration interaction in doubly excited states of 2-electron systems. He has also been examining the use of unrestricted Hartree-Fock wave functions in the study of electron correlation in atomic systems. In this he has attained some interesting results which show that this approach can be used to obtain a perturbation expansion containing terms of order $Z^{-\frac{1}{2}}$. These terms account for about ninety percent of the total radial correlation in the second order ground state energy of atoms such as helium. When these pieces of work by Dr. Stewart reach a more complete form copies will be forwarded to NASA.

NASA's support in this contract has assisted greatly in our continued development of aspects of quantum mechanical collision theory associated with chemical rearrangements and other heavy-particle collision processes. One of our most recent pieces of work, reference 13, was stimulated by some very recent experimental results in our laboratories, and the development of the theory of charge exchange will continue to be carried out in closest collaboration with the experiments. The charge exchange work is also very closely related to other items which are being studied in this program, notably, the study of collision

lifetimes and orbiting connected with the mechanism of 3-body atom-atom recombinations.

One aspect of the program we have been carrying out which we deem of particular importance is the attempt to examine both the quantum mechanical and the classical aspects of collision problems in close juxtaposition. There is no doubt that classical approximations are often extremely valuable but it is also true that they are too often used without considering their limitations. It is our hope that an approach which is focused on a parallel development will show both the limitations and the regions of validity of the classical approximations, and will provide methods for estimating and correcting for the errors of the classical approach. This is particularly important in connection with the heavy-particle collisions that are typical of chemical reactions, since these involve such a large number of partial waves that full scale quantum calculations are still extremely difficult.

## III PERSONNEL AND RELATED ACTIVITIES

The following personnel have contributed to this program. Dr. F. T. Smith, Dr. R. C. Whitten, and Dr. R. P. Marchi of the Stanford Research Institute staff and Dr. A. L. Stewart from the Queen's University of Belfast, who is participating as a visiting scientist. In addition, we have had other visitors for a shorter period of time including Dr. Takashi Ohmura of Tokyo University and Dr. Charles Curtiss of the University of Wisconsin.

In the fall of 1963 we initiated a series of informal seminars related to the theory of atomic and molecular processes. The following talks were given during the period October 22, 1963 to January 7, 1964.

Oct. 22 — Dr. A. Stewart, SRI, on leave from the Queen's University of Belfast, Belfast, North Ireland. "Some Recent Calculations on the Properties of Atomic Lithium and the Isoelectronic Ions."

| | |
|---|---|
| Oct. 29 | Dr. T. Ohmura, SRI, Visiting Scientist, Tokyo University of Japan<br>"Wave Packet Theory of Scattering." |
| Nov. 5 | Dr. T. Ohmura, SRI<br>"Free-Free and Bound-Free Transitions of $H^-$." |
| Nov. 12 | Dr. M. Mittleman, LRL, Livermore, California.<br>"Charge Exchange Collisions." |
| Nov. 19 | Dr. G. Gioumousis, Shell Development Corporation.<br>"Rotational Relaxation of $H_2$ with Regard to NMR." |
| Nov. 26 | Dr. F. Smith, SRI.<br>"Orbiting Collisions." |
| Dec. 3 | Dr. A. Stewart, SRI.<br>"Calculations of Atomic Properties Using Perturbation Theory." |
| Dec. 10 | Dr. Enrico Clementi, IBM, San Jose.<br>"Hartree-Fock Relativistic and Correlation Energy in Atoms and Small Molecules." |
| Dec. 17 | Professor Bruce Mahan, Chemistry Dept., University of California, Berkeley.<br>"Charge Recombination in Gases." |
| Jan 7 | Dr. Richard Brewer, IBM, San Jose.<br>"Optical Pumping and Gas Phase Collisions." |

Felix T. Smith
Senior Physical Chemist

FTS:tf

Approved:

Charles J. Cook, Director
Chemical Physics Division

## REFERENCES


1. F. T. Smith, Quantum Mechanics of Molecular Rearrangements: Collision Theory in Chemical Kinetics, Stanford Research Institute Report dated July 25, 1960.

2. F. T. Smith, Lifetime Matrix in Collision Theory, Phys. Rev. 118, 349 (1960).

3. F. T. Smith, Generalized Angular Momentum in Many-Body Collisions, Phys. Rev. 120, 1058 (1960).

4. F. T. Smith, A Symmetric Representation for Three-Body Problems. I. Motion in a Plane, J. Math. Phys. 3, 735 (1962).

5. F. T. Smith, Collision Lifetimes in Many-Body Processes, Phys. Rev. 130, 394 (1963).

6. R. C. Whitten, Three-Particle Scattering. I. Planar Case, J. Math. Phys. 4 (1963).

7. R. C. Whitten, Three-Particle Scattering. II. In Space (Preprint) Stanford Research Institute, Menlo Park.

8. F. T. Smith, Scattering Matrix and Chemical Reaction Rates, J. Chem. Phys. 36, 248 (1962).

9. F. T. Smith, Collision Lifetimes and the Thermodynamics of Real Gases, J. Chem. Phys. 38, 1304 (1963).

10. F. T. Smith, On the Quantum Virial Expansion, Phys. Rev. 131, 2803 (1963).

11. F. T. Smith, Three-Body Collision Rates in Atomic Recombination Reactions, Discussions Faraday Soc. 33, 186 (1962).

12. F. T. Smith, Collision Lifetimes, Phase Shifts and Orbiting Phenomena, Preliminary Draft dated Nov. 1, 1963.

13. F. T. Smith, Symmetric Charge Exchange at Low Energy, Preliminary Draft dated Jan. 7, 1964.